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(54) Title: AQUEOUS LIQUID AUTOMATIC DISHWASHING DETERGENT COMPOSITION HAVING BROMINE AND CHLORINE BLEACH

(57) Abstract

An aqueous liquid automatic dishwashing detergent product having improved cleaning performance against starch based soil without a significant detrimental affect on protein based soil removal, and a process for achieving improved cleaning performance against starch based soil without a significant detrimental affect on protein based soil removal from dishware during automatic dishwashing are disclosed. The aqueous liquid automatic dishwashing detergent product comprises, by weight, a combination of hyprochlorite bleaching species and hypobromite bleaching species. The bleaching species are present in an amount sufficient to deliver no greater than about 5 % by weight available halogen. The hyprobromite bleaching species and the hyprochlorite bleaching species are present in a molar ratio in a range of from about 1:1 to about 1:20, hyprobromite bleaching species to hyprochlorite bleaching species. The hyprobromite bleaching species are generated from a water soluble bromide source. The water soluble bromide source is free of a water insoluble protective coating.

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# AQUEOUS LIQUID AUTOMATIC DISHWASHING DETERGENT COMPOSITION HAVING BROMINE AND CHLORINE BLEACH

## TECHNICAL FIELD

The present invention relates to an aqueous liquid automatic dishwashing detergent composition. More particularly, the invention relates to an aqueous liquid automatic dishwashing detergent composition having a bromine and chlorine bleach system for delivering outstanding removal of starch based soil without any detrimental affect on the removal of protein based soil.

## BACKGROUND OF THE INVENTION

A key requirement of any liquid automatic dishwashing (ADW) detergent product is its ability to breakdown and remove dried, cooked on and burnt on soils from dishware, china, silverware, glassware and the like, referred generally hereinafter as dishware, for brevity. The soils that are typically deposited on such dishware include proteinaceous soils and starchy soils. While the ability of chlorine bleach based liquid dishwashing detergents to breakdown protein based soils is quite good and well documented in the art, the ability of chlorine bleach to breakdown certain starch based soils suffers from some limitations and thus leaves much room for improvement. In fact, because starch based soils are one of the key types of soils that consumers have to contend with in their quest for clean dishware, it has been an objective of the inventors to devise a composition that delivers a level of starch based soil removal which has heretofore been not possible, without detrimentally affecting the protein based soil removal.

The performance of bromine bleach based liquid ADW composition in the removal of protein based soils is not so good and this inability of bromine bleach to remove protein based soils is also well documented in the art. However, the ability of bromine bleach in removal of starch based soils is impressive, particularly when the composition also has high alkalinity.

In the past, it has also been recognized that as opposed to liquid ADW compositions, enzymes used in non-liquid detergents are effective against both protein based and starch based soil removal. However, enzyme based non-liquid detergents require an additional amount of time before an enzyme based detergent composition begins to operate at maximum efficiency. In the context of liquid ADW compositions, enzyme based liquid compositions are not stable in the presence of oxygen bleach. Enzyme based liquid ADW compositions are also incompatible with chlorine bleach and in general, it is safe to say that enzyme based liquid ADW compositions suffer from severe lack of enzyme compatibility with the chlorine and oxygen bleaching systems present in the liquid formulation.

Other researchers in this field have also experimented with dual-bleach systems. Particularly, the use of dual bleach systems, such as chlorine and bromine bleaches is known in the art. However, it has heretofore been understood by those skilled in the art, that to use a bromine bleach in conjunction with a chlorine bleach in a liquid ADW composition, the source of the bromine bleach has to be substantially insoluble in water or at the very least sparingly soluble in water. It has been heretofore understood that a water soluble bromine bleach source must be coated with a water insoluble coating, which dissolves only at higher temperatures, such as above 100 degrees F, which are commonly encountered in the wash solution. It has heretofore been understood by those skilled in the art that the hypobromite bleaching species must be generated in the wash solution only and that any "in situ" generation of hypobromite, i.e., generation of active hyprobromite in the liquid ADW product is detrimental to the storage stability of the liquid ADW product.

The inventor of the subject invention has surprisingly discovered that there is no need that the bromine source be water-insoluble or water-insoluble. The inventor of the subject invention has also discovered that if a water-soluble bromine source is used, such as alkali and alkaline earth metal bromides, it is no longer essential that such a water-soluble bromine source be coated with a water-insoluble coating which melts only at the temperature in the wash solution of the automatic dishwashing machine. This critical discovery has simplified that formulation of dual bleach systems, which can now use water-soluble bromine sources without any coating, a feature heretofore believed to be impossible to attain without sacrificing the liquid ADW product stability. This has enabled the formulation of dual bleach aqueous liquid ADW products that offer improved starch removal performance across all temperature ranges encountered in an automatic dishwasher, even when cold water is used.

It has thus been extremely desirable to have a thixotropic aqueous liquid automatic dishwashing detergent composition that not only delivers outstanding removal of starch based soil without any detrimental affect on protein based soil removal, but is importantly, stable in storage. When a dual bleach system using hypobromite and hypochlorite bleaching species is used, it has very much been desirable to have a thixotropic aqueous liquid automatic dishwashing detergent composition that not only does not require the source of hypobromite bleaching species to be water-insoluble or water-sparingly soluble in order to be stable. It has been desirable to have a liquid ADW product using a dual bleach system of bromine and chlorine bleaching species wherein there is no need to coat a water-soluble bromine bleach source with a water-insoluble coating that melts at the temperature in excess of 100 degrees F. It has also been desirable to have a stable thixotropic aqueous liquid automatic dishwashing detergent composition wherein

the hypobromite bleaching species is generated "in situ" in the liquid ADW product itself, thus allowing for better colder temperature, i.e., temperatures less than 100 degree F, starch removal performance of the liquid ADW product.

The inventor of the subject invention has discovered that the above problem is solved by formulating an aqueous liquid ADW composition that utilizes a unique combination of hypochlorite bleach and hyprobromite bleach in a pre-selected ratio, wherein the bromine source is water-soluble. The aqueous liquid ADW composition of the present invention delivers excellent removal of starch based soil and without any detrimental affect on protein based soil removal. Because the hypobromite bleaching species is generated "in situ", i.e., in the liquid ADW product itself, the starch removal performance of the liquid ADW product is immediate and improved even at temperature less than 100 degrees F as compare to those liquid ADW products wherein water-insoluble, water-sparingly soluble, or water-soluble-but-coated bromine sources are used.

Thus the present invention aims to solve all of the aforementioned problems.

## BACKGROUND ART

U.S. Patent No. 5,164,106 discloses a non-aqueous liquid automatic dishwasher detergent composition containing a dual bleach system.

U.S. Patent No. 5,108,641 discloses an aqueous liquid automatic dishwasher detergent composition containing a dual bleach system.

## SUMMARY OF THE INVENTION

The invention meets the needs above by providing an aqueous liquid automatic dishwashing detergent product having improved cleaning performance against starch based soil without a significant detrimental affect on protein based soil removal, and a process for achieving improved cleaning performance against starch based soil without a significant detrimental affect on protein based soil removal from dishware during automatic dishwashing.

In one aspect of the present invention, the aqueous liquid automatic dishwashing detergent product comprises, by weight, a combination of hyprochlorite bleaching species and hypobromite bleaching species. The bleaching species are present in an amount sufficient to deliver no greater than about 5% by weight available halogen. The hyprobromite bleaching species and the hyprochlorite bleaching species are present in a molar ratio in a range of from about 1:1 to about 1:20, hyprobromite bleaching species to hyprochlorite bleaching species. The hyprobromite bleaching species are generated from a water soluble bromide source. The water soluble bromide source is free of a water insoluble protective coating.

In another aspect of the present invention, the process comprises the steps of (a) providing an aqueous liquid automatic dishwashing detergent composition as set forth above, and (b) washing the dishware by an automatic dishwashing method.

The aqueous liquid automatic dishwashing detergent product of the present invention not only delivers outstanding removal of starch based soil without any detrimental affect on protein based soil removal, but is importantly, stable in storage, despite the generationof the hypobromite bleaching species "in situ" in the liquid product.

## DETAILED DESCRIPTION OF THE INVENTION

In the preferred embodiment of the present invention, the aqueous liquid automatic dishwashing detergent product comprises, by weight, a combination of hyprochlorite bleaching species and hypobromite bleaching species. The bleaching species are present in an amount sufficient to deliver no greater than about 5% by weight available halogen. The hyprobromite bleaching species and the hyprochlorite bleaching species are present in a molar ratio in a range of from about 1:1 to about 1:20, hyprobromite bleaching species to hyprochlorite bleaching species. The hyprobromite bleaching species are generated from a water soluble bromide source. The water soluble bromide source is free of a water insoluble protective coating.

The mole ratio of the bromide to available chlorine is critical and is desirable in a range of from about 1:1 to about 1:20, more desirable in a range of from about 1:2 to about 1:7, preferably in a range of from about 1:2 to about 1:6, more preferably in a range of from about 1:3 to about 1:6 and most preferably, about 1:4, hyprobromite bleaching species to hyprochlorite bleaching species.

In accordance with the present invention, the aqueous liquid automatic dishwashing detergent product is prepared by incorporating a water soluble source of hyprobromite bleaching species in a dishwasher composition containing a hyprochlorite bleaching species.

Thixotropic cleaning compositions are highly viscous in a quiescent state and have relatively high yield stress values. When subjected to shear stresses, however, such as being shaken in a container or squeezed through an orifice, they quickly fluidize and upon cessation of the applied shear stress, quickly revert to a high viscosity state. The thixotropic aqueous liquid ADW compositions are low foaming, they are readily soluble in the washing medium and most effective at pH values best conducive to improved cleaning performance, such as in a range of desirably from about pH 9.0 to about pH 13.0, preferably from about pH 9.0 to about pH 12.0.

The thickness or viscosity of the liquid product may be altered by the addition of a fatty acid, metal salt of a fatty acid and/or clay thixotropic thickener. Desirably, about 0.02% to about 3% by weight of a fatty acid.thixotropic thickener is added to the liquid detergent

composition. Alternatively, in addition to about 0.02% to about 3% by weight of a fatty acid thixotropic thickener, from about 0.1% to about 3% of an inorganic thixotropic clay thickener may be also be added to the liquid detergent composition. Still alternatively, the aqueous liquid detergent composition may include from about 1.5% to about 8% of a fatty acid thixotropic thickener.

In a preferred embodiment of the invention, the physical stability of the liquid product may be improved and the thickness of the liquid product may be altered by the addition of a cross linking polyacrylate thickener to the liquid detergent product as a thixotropic thickener. The polyacrylate thickener is added in an amount sufficient to achieve a yield stress in a range of from about 10 Pa to about 30 Pa and a static viscosity of at least 5000 $l.s^{-1}$. The aqueous thixotropic liquid automatic dishwashing detergent product exhibits rheological properties are evaluated by testing product viscosity as a function of shear rate. The compositions exhibit higher viscosity at a low shear rate and lower viscosity at a high shear rate. In practical terms, this means improved pouring and processing characteristics as well as less leaking in the machine dispenser-cup, compared to prior liquid or gel ADW compositions. In terms of apparent viscosity, it has been ascertained that so long as the viscosity at room temperature (22 °C ± 1°C) measured in a Brookfield Viscosimeter HATD, using a number 4 spindle at 20 rpm, is in a range of about 20,000 to about 30,000 cps, depending upon the formula and the thickener used, the composition can be readily shaken so that a thixotropic composition can be easily "fluidized" or "liquefied" to allow the product to be dispensed through a conventional squeeze tube bottle or other convenient dispenser.

The present invention is based upon the surprising discovery that outstanding removal of starch based soil without any detrimental affect on protein based soil removal can be attained by adding to the thixotropic aqueous liquid detergent composition, hyprobromite bleaching species and hypochlorite bleaching species in a molar ratio of hyprobromite:hypochlorite in a range of from about 1:1 to about 1:20. The physical stability, i.e., resistance to phase separation and settling, is improved by adding to the composition, a small effective amount of a thixotropic thickener and stabilizing agent, such as the crosslinked polyacrylate thickener as mentioned before. Further, the liquid product is stable despite the generation of the hyprobromite species in situ, rather than in the wash solution of the automatic dishwashing machine, and despite the water soluble nature of the bromide source, and further despite the fact that the water soluble bromide source is not encapsulated, either fully or partially, or enclosed in any manner, by a water insoluble protective coating or barrier.

Hypochlorite Bleaching Species

Hypochlorite generating compounds suitable for use in the compositions of the present invention are those water soluble dry solid materials which generate hypochlorite ion on contact with, or dissolution in, water. The preferred hypochlorite compounds are alkali and alkaline earth hypochlorites. The hypochlorite generating compounds are generally soluble in the product composition. Examples thereof are the dry, particulate heterocyclic N-chlorimides such as trichlorocyanuric acid, dichlorocyanuric acid and salts thereof such as sodium dichlorocyanurate and potassium dichlorocyanurate. The corresponding dichloroisocyanuric and trichloroisocyanic acid salts can also be used. Other N-chloroimides may be used such as N-chlorosuccinimide, N-chloromalonimide, N-chlorophthalimide and N-chloronaphthalimide. Additional suitable N-chloroimides are the hydantoins such as 1,3-dichloro-5,5-dimethylhydantion; N-monochloro-C,C-dimethylhydantoin; methylene-bis (N-chloro-C,C-dimethylhydantoin); 1,3-dichloro-5-methyl-5-isobutylhydantoin; 1,3-dichloro-5-methyl-5-ethylhydantoin; 1,3-dichloro-5,5-diisobutylhydantoin; 1,3-dichloro-5-methyl-5-n-amylhydantoin; and the like. Other useful hypochlorite-liberating agents are trichloromelamine and dry, particulate, water soluble anhydrous inorganic salts such as lithium hypochlorite and calcium hypochlorite. The hypochlorite liberating agent may, if desired, be a stable, solid complex or hydrate such as sodium p-toluene-sulfo-chloramine-trihydrate (choramine-T), sodium benzene-sulfo-chloramine-dihydrate, calcium hypochlorite tetrahydrate, or chlorinated trisodium phosphate containing no more than 4% available chlorine produced by combining trisodium phosphate in its normal $Na_3$ $PO_4 12H_2 0$ form and an alkali metal hypochlorite (e.g., sodium hypochlorite).

In the preferred embodiment of the present invention, the hypochlorite bleaching species are present in a sufficient amount of deliver in a range of 0.5% to 4% by weight, available chlorine. Specific amounts of the desired hypochlorite species can be determined by one skilled in the art without undue experimentation to attain the aforementioned available chlorine. For example, a composition containing about 7.4 to 22.20% by weight of sodium hypochlorite contains about 1 to 3% by weight of available chlorine.

Desirably the proportion of chlorine-liberating compound employed will be such as to yield a product which contains desirably no more than 4% available chlorine.

Hypobromite Bleaching Species

The present invention hinges on the important discovery that the bromide compounds that can be used in accordance with the present invention are those that are water soluble. The invention expressly precludes the need for water insoluble or only sparingly water soluble bromide compounds that are soluble in the larger volume of the dishwasher wash solution at wash temperatures of 100 °F to 140 °F. It is expressly preferred, for the sake of simplicity and

economy, that the water soluble bromide compounds are free of a protective water-insoluble coating of any form or manner.

Water soluble bromide salts are best suited for aqueous liquid ADW compositions because they result in a stable to storage liquid product despite the formation of the active hypobromite in the detergent liquid product generated in situ therein, rather than in the wash cycle at higher temperature and increased water volume in the dishwasher. It has been discovered that bromide salts that are soluble in the aqueous liquid ADW product can be used and they do not degrade the shelf life of the liquid ADW product.

In the preferred embodiment of the invention, readily water soluble bromide compounds, such as alkali and alkaline earth metal bromides are used. Preferably, sodium bromide is used. These readily soluble bromide compounds are preferably not encapsulated in a protective coating that is insoluble or only sparingly soluble in the liquid product. Thus, a balanced aqueous liquid detergent product is obtained which contains an effective amount of the bromide which reacts with the hypochlorite to form a sufficient amount of hypobromite to remove the starchy carbohydrate soil and leaves a sufficient amount of hypochlorite ion in the wash bath to remove the proteinaceous soil. Thus, the aforementioned weight percent available halogen and the mole ratio of bromide to available chloride are important features of the present invention.

Thixotropic Thickeners

The thixotropic thickeners or suspending agents that can be used in accordance with the present invention to provide the aqueous medium with thixotropic properties may be organic, for example, fatty acid or fatty acid metal salts or inorganic colloid forming clay materials. The thixotropic thickeners should be stable to high alkalinity and stable to chlorine bleach compounds such as sodium hypochlorite. The useful thixotropic thickeners comprise the fatty acids, the fatty acid polyvalent metal salts and the inorganic, colloid-forming clays of smectite and/or attapulgite types. Thus, examples of the fatty acids which can be used as thickeners include, for example, decanoic acid, lauric acid, dodecanoic acid, palmitic acid, myristic acid, stearic acid, oleic acid, eicosanoic acid, tallow fatty acid, coco fatty acid, soya fatty acid and mixtures of these acids. Stearic acid and mixed fatty acids, e.g. coco fatty acid, are also useful. There may also be used in the present invention the conventional inorganic thixotropic clay thickeners. The clay thickeners may be used in small amounts in combination with the fatty acid thickeners or in combination with fatty acid polyvalent metal salt thickeners. The clay thickeners, however, may be used by themselves as the thixotropic thickeners. Useful clay thickeners comprise the inorganic, colloid forming clays of smectite and/or attapulgite types. Smectite clays include montmorillonite (bentonite), hectorite, attapulgite, smectite, saponite, and

the like. Montmorillonite clays are also useful and are available under tradenames such as Thixogel (Registered Trademark) No. 1 and Gelwhite (Registered Trademark) GP, H, etc., from Georgia Kaolin Company; and Eccagum (Registered Trademark) GP, H, etc., from Luthern Clay Products.

In a preferred embodiment of the invention, the thickener used is a cross linking polyacrylate thickener, added to the liquid detergent product. The polyacrylate thickener is added in an amount sufficient to achieve a yield stress in a range of from about 10 Pa to about 30 Pa and a static viscosity of at least 5000 $l.s^{-1}$.

PH adjusting components

It is preferred herein that the pH at about 1% dilution with de-ionized water, by weight, of the aqueous thixotropic liquid ADW composition product be at least about 9.0, more preferably from about 10.5 to 12.0 and most preferably at least about 11.7. The pH adjusting components are desirably selected from sodium or potassium carbonate or sesquicarbonate, sodium or potassium citrate, citric acid, sodium or potassium bicarbonate, sodium or potassium borate, sodium or potassium hydroxide, and mixtures thereof. NaOH is a preferred ingredient for increasing the pH to within the above ranges. Other preferred pH adjusting ingredients are potassium hydroxide, potassium silicate, sodium silicate, sodium carbonate, potassium carbonate, and mixtures thereof.

Low Foaming Non-ionic Surfactant

The liquid nonionic surfactant detergents that can be used to practice the present invention are preferably chlorine bleach stable low foaming non-ionic surfactants. In the preferred embodiment, such surfactants are present in a range of from about 0.1% to about 10% by weight of the liquid composition. The chlorine bleach stable low foaming nonionic surfactants are desirably selected from the group consisting of chloride bleach stable alkoxylated alcohols, and mixtures thereof. Such surfactants are generally known to one skilled in the art and need not be elaborated here, for purposes of brevity.

Other ingredients

The aqueous liquid automatic dishwashing detergent composition optionally also contains from about 0.5% to about 20% of a dispersant polymer selected from the group consisting of polyacrylates and polyacrylate copolymers, and from about 0.1% to about 5% of a chlorine bleach stable foam suppressant. Such foam suppressants are well known to those skilled in the art.

In an embodiment of the invention an aqueous liquid concentrate automatic dishwashing detergent composition is formulated using the below named ingredients, as set forth in Example A.

EXAMPLE A

| Ingredient | weight % active |
|---|---|
| Sodium Tripolyphosphate | 17.50 |
| Sodium Silicate | 5.16 |
| Potassium hydroxide | 3.58 |
| Sodium hydroxide | 1.95 |
| Polyacrylate polymer | 1.01 |
| Nitric Acid | 0.0117 |
| Perfume | 0.03 |
| Sodium Silicate | 0.95 |
| Sodium Benzoate | 0.75 |
| Sodium hypochlorite | 1.15 |
| Sodium Bromide | 0.80 |
| Water | Balance |
| TOTAL | 100.00 |

Accordingly, having thus described the invention in detail, it will be obvious to those skilled in the art that various changes may be made without departing from the scope of the invention and the invention is not to be considered limited to what is described in the specification.

WHAT IS CLAIMED IS:

1. An aqueous liquid automatic dishwashing detergent product having improved cleaning performance against starch based soil without a significant detrimental affect on protein based soil removal, characterized by, by weight:

(a) a combination of hyprochlorite bleaching species and hypobromite bleaching species, said bleaching species being present in an amount sufficient to deliver no greater than 5% by weight available halogen;

(b) said hyprobromite bleaching species and said hyprochlorite bleaching species being present in a molar ratio in a range of from 1:1 to 1:20, hyprobromite bleaching species to hyprochlorite bleaching species;

(c) said hyprobromite bleaching species being generated from a water soluble bromide source; and

(d) said water soluble bromide source being free of a water insoluble protective coating.

2. An aqueous liquid detergent product according to claim 1, wherein said hyprochlorite bleaching species is selected from the group consisting of chlorocyanurates, chloroisocyanurates, dichloroisocyanurates, and alkali and alkaline earth metal hypochlorites.

3. An aqueous liquid detergent product according to claims 1-2, wherein said hyprochlorite bleaching species is selected from the group consisting of alkali and alkaline earth metal hypochlorites.

4. An aqueous liquid detergent product according to claims 1-3, wherein said water soluble bromide source is selected from the group consisting of alkali and alkaline earth metal bromides.

5. An aqueous liquid detergent product according to claims 1-4, wherein said hypobromite bleaching species is generated in situ in said aqueous liquid detergent product.

6. An aqueous liquid detergent product according to claims 1-5, wherein said water soluble bromide source of said hypobromide bleaching species is sodium bromide.

7. An aqueous liquid detergent product according to claims 1-6, wherein said hyprobromite bleaching species and said hyprochlorite bleaching species are present in a molar ratio in a range of from 1:2 to 1:6, hyprobromite bleaching species to hyprochlorite bleaching species.

8. An aqueous liquid detergent product according to claims 1-7, wherein said hyprobromite bleaching species and said hyprochlorite bleaching species are present in a molar ratio in a range of from 1:3 to 1:6, hyprobromite bleaching species to hyprochlorite bleaching species.

9. An aqueous liquid detergent product according to claims 1-8, including a pH adjusting component, wherein said pH adjusting component is selected from the group consisting of sodium or potassium carbonate or sesquicarbonate, sodium or potassium citrate, citric acid, sodium or potassium bicarbonate, sodium or potassium borate, sodium or potassium hydroxide, and mixtures thereof.

10. A process for achieving improved cleaning performance against starch based soil without a significant detrimental affect on protein based soil removal from dishware during automatic dishwashing, characterized by the steps of:

(a) providing an aqueous liquid automatic dishwashing detergent product according to claim 1; and

(b) washing said dishware by an automatic dishwashing method.

# INTERNATIONAL SEARCH REPORT

Inte. ..ational Application No
PCT/US 99/28995

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/395

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | US 5 108 641 A (AHMED FAHIM U ET AL)<br>28 April 1992 (1992-04-28)<br>cited in the application<br>examples 1-6<br>claims 1-16 | 1-10 |
| X | WO 97 20909 A (PETRI MARCO ;NA HENRY CHENG (US); PROCTER & GAMBLE (US))<br>12 June 1997 (1997-06-12)<br>examples 1-7 | 1-9 |
| X | US 4 755 354 A (TRINH TOAN ET AL)<br>5 July 1988 (1988-07-05)<br>column 2, line 38 -column 3, line 22<br>column 5, line 17 - line 22 | 1-9 |

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[X] Further documents are listed in the continuation of box C.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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